

Aerosol Chemical Species and Volatile Organic Compounds at Barrow

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INTRODUCTION

In winter and spring, a dense haze occurs in the Arctic. This "Arctic haze" contains large amounts of particulate pollutants, such as soot, sulfate, organics, and heavy metals, and gaseous pollutants, such as sulfur dioxide, nitric acid, and volatile organic compounds (VOCs) [Shaw, 1995]. The soot particles strongly absorb solar radiation, which changes the thermal structure of the Arctic atmosphere. Deposited soot reduces snow surface albedo, which perturbs the radiation budget in the Arctic [Blanchet, 1989; Aoki *et al.*, 1998]. In addition, heavy metals, such as lead, vanadium, and arsenic, and VOCs, such as benzene, trichloroethylene, and tetrachloroethylene, in the haze attract concern with respect to their possible human health impacts because they are known carcinogenic compounds.

In this study results are reported from the measurement of the concentrations of chemical species in fine particles (aerosols less than 2 μm in diameter) and VOCs collected at the CMDL Barrow Observatory in 1999-2001. The measurement results serve as basic data with which to evaluate possible effects of pollutants on climate, human health, and ecosystems in the Alaskan Arctic.

MATERIALS AND METHODS

Atmospheric fine particles were collected on Teflon filters (Sumitomo Electric Industry Inc., FP-1000, 47 mm) and quartz fiber filters (Pallflex 2500 QAT-UP, 47 mm) simultaneously by drawing outdoor air through a cyclone separator with a 50% cut point of 2- μm diameter at a flow rate of 20 L min^{-1} . Each sample was integrated over a 2-wk period from August 1999 through June 2001. Ionic components of aerosols collected on the Teflon filter were extracted ultrasonically with distilled-deionized water and analyzed with an ion chromatograph (IC, Yokogawa Analytical Systems) for anions (model IC 7000, column Excelpack ICS0-A23) and for cations (model ICS-C25). Metal components of aerosols on the Teflon filter were extracted with a mixed solution of nitric acid and hydrofluoric acid and analyzed with an inductively coupled plasma mass spectrometer (ICP-MS, Yokogawa Analytical Systems, HP 4500). The carbonaceous components of aerosols (elemental and organic carbon) on the quartz fiber filters were determined by sample combustion in a condensation nuclei (CN) coder at 850°C coupled with a flame ionization detector (FID) with a nickel catalyst methanizer [Ohta and Okita, 1984].

VOCs were sampled once a month from March 2000 through August 2001. Air was drawn into a collection tube (Carbotrap 317, SUPELCO) at a flow rate of 100 mL min^{-1} for 2 hours. The collected VOCs were thermally desorbed and injected into a mass spectrometer using a Thermal Deposition Cold Trap (TCT) injector.

RESULTS AND DISCUSSION

Two-week average concentrations of chemical species in fine particles in the atmosphere collected at CMDL, Barrow, from August 1999 through June 2001 are presented in Figure 1. The concentrations of species ranged as follows: elemental carbon (EC), 0.001-0.32 $\mu\text{g C m}^{-3}$; organic carbon (OC), 0.20-0.69 $\mu\text{g C m}^{-3}$; sulfate (SO_4^{2-}), 0.09-1.7 $\mu\text{g m}^{-3}$; nitrate (NO_3^-), 0.00-0.15 $\mu\text{g m}^{-3}$; chloride (Cl^-), 0.001-1.81 $\mu\text{g m}^{-3}$; ammonium (NH_4^+), 0.00-0.14 $\mu\text{g m}^{-3}$; seasalt cations (S.S.C.), 0.007-1.8 $\mu\text{g m}^{-3}$; and soil particles (Soil), 0.003-0.25 $\mu\text{g m}^{-3}$. The concentrations of S.S.C. and Soil were calculated respectively as follows:

$$[\text{S.S.C.}] = 1.194 \times [\text{Na}^+] \text{ and } [\text{Soil}] = 12.35 \times [\text{Al}]$$

The total amount of the chemical species increased in winter and spring (November-April) and decreased in summer and autumn (May-October). In particular, concentrations of EC and SO_4^{2-} increased in winter and spring, in concert with the occurrence of Arctic haze [Shaw, 1995].

In preparation for the OC measurements, the quartz fiber filters were pretreated by heating at 850°C in air for 1 hour to remove organic contaminants. But, due to the heating, the clean surfaces of the quartz fiber filters easily absorbed gaseous organics in the sampling air. Thus the OC concentration reported herein may be overestimated.

Figure 2 shows 2-wk average concentrations of metal components of fine particles in the atmosphere at Barrow. The concentrations (ng m^{-3}) of species ranged as follows: vanadium (V), 0.02-0.82; manganese (Mn), 0.00-1.73; copper (Cu), 0.00-0.83; zinc (Zn), 0.00-6.48; arsenic (As), 0.00-1.97; and lead (Pb), 0.06-6.68. These concentrations increased in winter and spring (November-April) and decreased in summer and autumn (May-October), similar to concentrations of EC and SO_4^{2-} , again due to Arctic haze. Concentrations of Zn and Pb, increased in January and February 2000 and January to May 2001. Zn and Pb are emitted mainly from solid waste incineration and automobile exhausts, respectively.

Table 1 shows atmospheric concentrations of VOCs from March 2000 through August 2001 at Barrow. The concentrations (ppbv) ranged as follows: chloroform (0.005-0.014); 1, 2-dichloroethane (0.00-0.012); carbon tetrachloride (0.00-0.11); ethylbenzene (0.008-0.11); m, p-xylene (0.01-0.15); styrene (0.006-0.092); o-xylene (0.007-0.096); 1-ethyl-3-methyl-benzene (0.002-0.04); 1, 3, 5-trimethylbenzene (0.002-0.11); 1, 2, 4-trimethylbenzene (0.008-0.50); and 1, 4-dichlorobenzene (0.001-0.057). Except for chloroform, 1, 2-dichloroethane, and carbon tetrachloride, concentrations of the other compounds had seasonal variations with spring maxima. Data from five of the compounds listed in Table 1 are plotted in Figure 3.

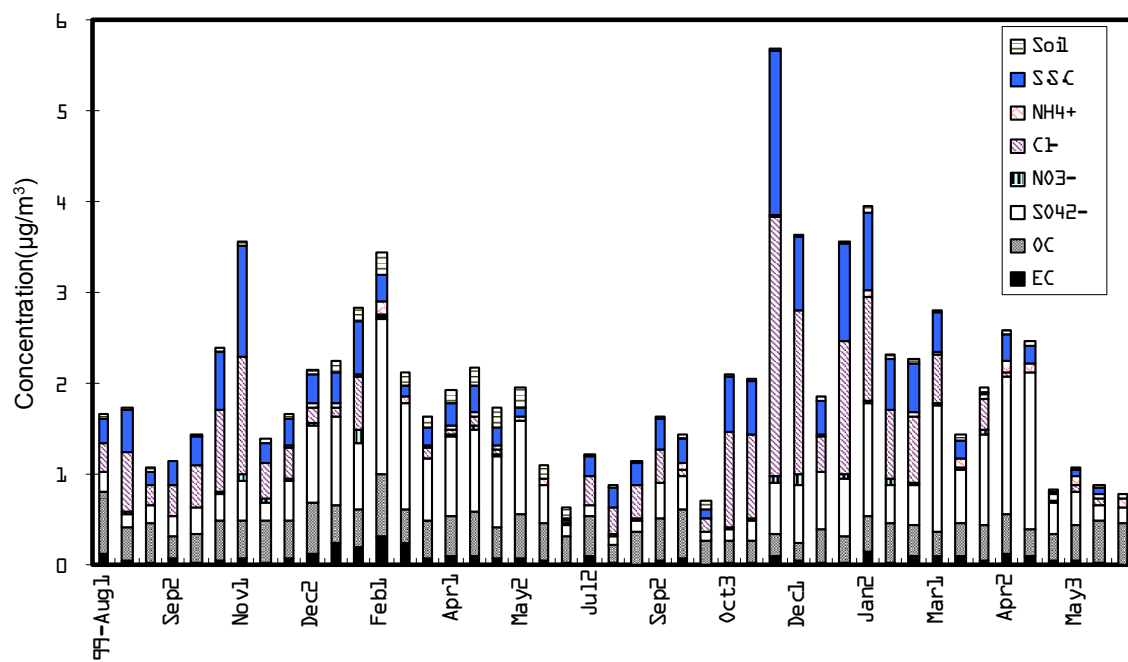


Fig. 1. Two-week average concentrations of chemical species in fine particles in the atmosphere at Barrow.

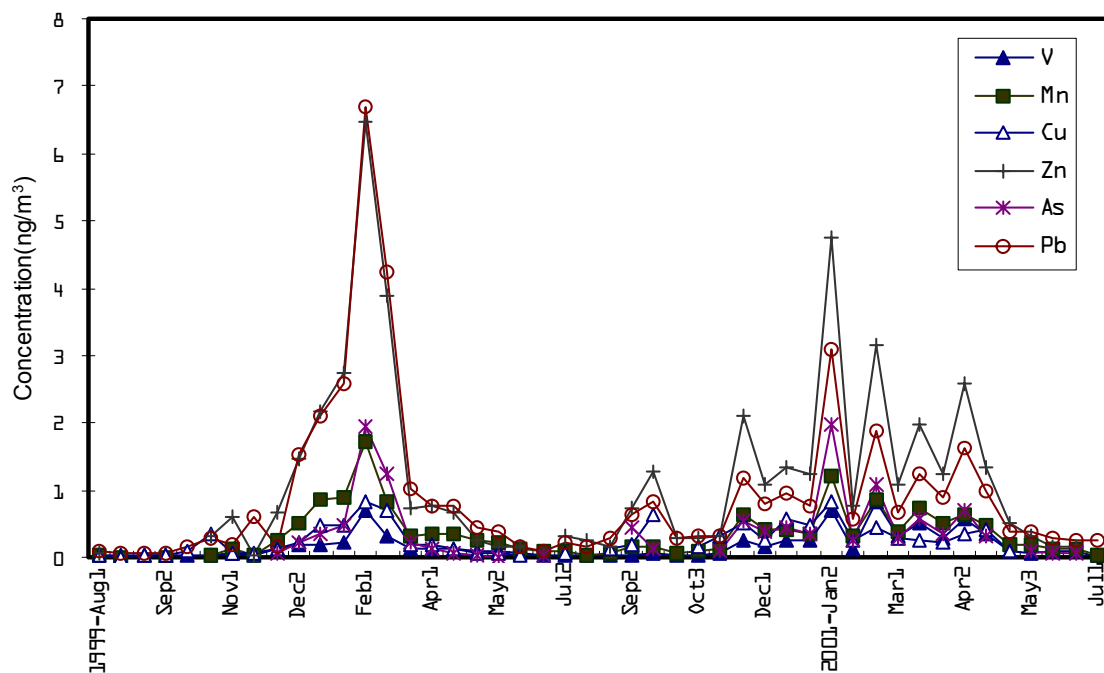


Fig. 2. Two-week average concentrations of metal components of fine particles in the atmosphere at Barrow.

TABLE 1. Concentrations of Volatile Organic Compounds (VOCs) in the Atmosphere at Barrow

Compound	Concentration (ppbv)									
	March-December 2000									
	March 9	March 30	April 27	May 26	June 26	July 26	Oct. 26	Nov. 15	Dec. 21	
Chloroform	0.012	0.012	0.013	0.011	0.013	0.013	0.011	0.014	0.010	
Ethane, 1,2-dichloro	0.007	0.007	0.009	0.006	0.004	0.006	0.005	0.005	0.007	
Carbon tetrachloride	0.060	0.064	0.083	0.075	0.051	0.088	0.073	0.065	0.092	
Ethylbenzene	0.064	0.068	0.049	0.052	0.008	0.009	0.027	0.024	0.062	
m,p-Xylene	0.120	0.126	0.084	0.094	0.012	0.011	0.043	0.036	0.091	
Styrene	0.044	0.075	0.081	0.073	0.006	0.009	0.029	0.028	0.048	
o-Xylene	0.090	0.096	0.054	0.059	0.009	0.007	0.026	0.021	0.064	
Benzene, 1-ethyl-3-methyl-	0.018	0.021	0.010	0.010	0.002	0.003	0.005	0.003	0.012	
Benzene, 1,3,5-trimethyl-	0.023	0.026	0.015	0.015	0.002	0.003	0.007	0.004	0.016	
Benzene, 1,2,4-trimethyl-	0.098	0.110	0.058	0.060	0.008	0.011	0.027	0.017	0.061	
Benzene, 1,4-dichloro-	0.002	0.007	0.035	0.011	0.001	0.008	0.005	0.002	0.023	
January-August 2001										
	Jan. 18	Feb. 26	March 30	April 25	May 18	June 15	July 18	Aug. 25		
Chloroform	0.011	0.013	0.011	0.008	0.008	0.005	0.008	0.008		
Ethane, 1,2-dichloro-	0.012	0.012	0.011	0.008		0.005				
Carbon tetrachloride	0.106	0.101	0.103	0.100	0.099		0.084	0.099		
Ethylbenzene	0.067	0.111	0.082	0.083	0.049	0.013	0.053	0.049		
m,p-Xylene	0.093	0.148	0.093	0.103	0.060	0.014	0.048	0.060		
Styrene	0.068	0.092	0.054	0.049	0.039	0.013	0.019	0.039		
o-Xylene	0.066	0.089	0.057	0.077	0.038	0.011	0.028	0.038		
Benzene, 1-ethyl-3-methyl-	0.040	0.023	0.010	0.022	0.010	0.004	0.005	0.010		
Benzene, 1,3,5-trimethyl-	0.111	0.034	0.015	0.046	0.015	0.006	0.006	0.015		
Benzene, 1,2,4-trimethyl-	0.498	0.127	0.058	0.210	0.058	0.025	0.023	0.058		
Benzene, 1,4-dichloro-	0.038	0.057	0.006	0.007	0.007	0.008	0.011	0.007		

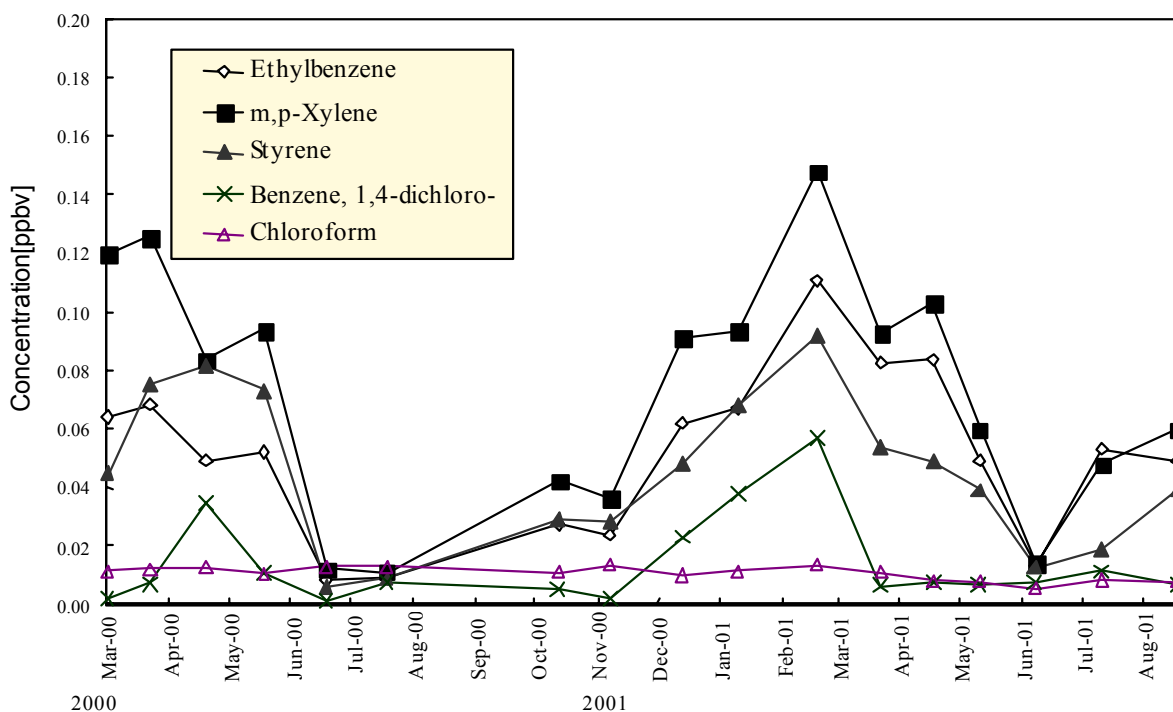


Fig. 3. Concentrations of VOCs in the atmosphere at Barrow.

Ethylbenzene is used as a solvent, and xylene, styrene, and other benzenes are emitted from automobile exhaust, reinforcing that these gases have been transported at least 6,000 miles from Eurasia. Since the VOCs were sampled only for 2 hours each sample day, the measured VOC concentrations inevitably depend on weather conditions and transport history. Thus wind direction, wind speed, and atmospheric stability must be checked on the days the VOCs were sampled, as well as the back trajectories for the sampling times, in order to better interpret the data.

REFERENCES

- Aoki, T., T. Aoki, M. Fukabori, and Y. Zaizen, Spectral albedo observation on the snow field at Barrow, Alaska, *Climate Monitoring and Diagnostics Laboratory Summary Report No. 24 1996-1997*, edited by D.J. Hofmann, J.T. Peterson, and R.M. Rosson, pp. 122-123, NOAA Environ. Res. Labs., Boulder, CO, 1998.
- Blanchet, J.-P., Toward estimation of climatic effects due to Arctic aerosols, *Atmos. Environ.*, 23, 2609-2625, 1989.
- Ohta, S., and T. Okita, Measurements of particulate carbon in urban and marine air in Japanese areas, *Atmos. Environ.*, 11, 2439-2445, 1984.
- Shaw, G.E., The Arctic haze phenomenon, *Bull. Am. Meteorol. Soc.*, 76, 2403-2413, 1995.